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(54) Method for making polysiloxane emulsions

Verfahren zur Herstellung von Polysiloxanemulsionen

Procédé de préparation d'emulsions de polysiloxane

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Description

The instant invention pertains to a method for making polysiloxane emulsions using what is commonly known as emulsion polymerization. The emulsions of this invention are produced from a mixture comprising at least one siloxane oligomer, cationic or anionic surfactant, nonionic surfactant, catalyst and water whereby the siloxane oligomer is reacted in the presence of water and the surfactants to form the polysiloxane emulsions. By using the method of the instant invention, it is feasible to produce oil free standard, fine and micro-emulsions.

Polysiloxane emulsions may be categorized by the size of the polysiloxane particles and the appearance of the emulsion. Typically three categories of silicone emulsions are recognized in the art - standard emulsions, fine emulsions and microemulsions. The term emulsion used herein encompasses the three individual types of silicone emulsions.

Silicone standard emulsions are characterized by a large particle size (typically greater than 300 nanometers) and appear to the human eye to be opaque (impenetrable to light). Silicone standard emulsions are most commonly identified as those having an intense white appearance. Silicone fine emulsions are characterized by a smaller particle size, from 300 to 140 nanometers and are identified as those compositions which visually may be slightly opaque to very slightly translucent (transmitting light but with distortion). Silicone microemulsions are characterized as those having a particle size of less than 140 nanometers and visually appear translucent to transparent (transmitting light without distortion).

Out of the three types of silicone emulsions, fine emulsions and microemulsions are the most desired due to their smaller particle size and higher stability. Microemulsions are further desired due to their translucent to transparent appearance. Because of these factors, microemulsions are more preferred and can be used in more applications than standard or fine emulsions.

Methods for making emulsions of polysiloxanes in water are well known in the art. The methods are generally classified in two categories: mechanical means and emulsion polymerization. Mechanical means usually entail taking the polysiloxane and using mechanical means such as homogenizers or vigorous agitation to emulsify the siloxanes in water. Typically a surfactant is added to the polysiloxane or water to aid the emulsification process.

Emulsion polymerization typically entails combining a reactive silicone oligomer, surfactant, polymerization catalyst and water. The mixture is stirred and the silicone oligomers are allowed to polymerize until a standard emulsion, fine emulsion or microemulsion is formed. Typically alkoxysilanes, which result in the formation of microemulsions or cyclic siloxanes, which result in the formation of fine and standard emulsions are used as the reactive monomers and oligomers. Combinations of the silicone reactants can also be used to form copolymers in the resulting emulsion.

Typical problems encountered with emulsion polymerization of cyclic siloxanes include the presence of an unemulsified silicone oil layer or very large (visible to the human eye) silicone oil droplets in the final emulsion produced. Using methods known in the art, complete elimination of the silicone oil layer is not achieved unless the cyclic siloxane is pre-emulsified using mechanical means prior to polymerization. Mechanical pre-emulsification of the cyclic siloxanes in water prior to emulsion polymerization is a common, well known practice to those skilled in the art. Also, when using cyclic siloxanes as the starting oligomer in methods known in the art, it is generally not possible to achieve a conversion of cyclic siloxane into polysiloxane polymer greater than amounts determined by the ring/chain equilibrium of the system. In other words, there will always be a certain level of cyclic siloxane present in the emulsion and this level is typically determined by the ring/chain equilibrium for the system.

EP-A 0 228 575 teaches a method for making polydiorganosiloxane microemulsions wherein first a pre-emulsion is prepared from polydiorganosiloxane, precursor, surfactant and water, then the pre-emulsion is added to a polymerization catalyst medium while mixing to form a clear, stable aqueous microemulsion, and in a third step the polymerization is carried out.

The methods known in the art using emulsion polymerization are limited as the resulting emulsions do not have a broad range of possible particle sizes. Further, the methods have narrow or no range in which they will produce oil-free (those containing no unemulsified silicone oil) emulsions unless pre-emulsification is employed.

It is an object of this invention to provide a method for making polysiloxane emulsions using emulsion polymerization.

It is further an object of this invention to provide a method for controlling the emulsion polymerization to produce a desired type of emulsion having a desired particle size and which is free of unemulsified silicone oil.

It is further an object of this invention to provide a method for producing stable, oil-free micro-emulsions without having to mechanically pre-emulsify the polysiloxane.

It is further an object of this invention to provide a single method which allows for the production of emulsions, fine emulsions and microemulsions.

It has been found that by controlling or specifying certain operating parameters in the method of the instant invention for the preparation of polysiloxane emulsions via emulsion polymerization, the type and particle size of emulsion resulting from the method can be controlled. It has also been found that by including a nonionic surfactant during the polymerization reaction that a stable, oil-free emulsion will result. The method of the instant invention can be used to

produce standard emulsions, fine emulsions and microemulsions. Emulsions with particle sizes greater than approximately 10 nanometers (nm) can be produced using the method of the instant invention. The operating parameters which have been shown to have specific importance in controlling the particle size include reaction temperature, amount and type of ionic (anionic or cationic) surfactant, amount and type of nonionic surfactant, amount of water, amount of catalyst and the optional presence of alcohols.

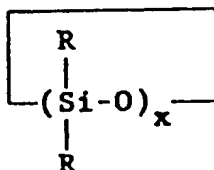
The method of the instant invention has been shown to produce stable, oil free (containing no unemulsified silicone oil) emulsions when the above identified reaction parameters are within certain limits. A stable, oil-free emulsion is one that is defined as an emulsion which does not contain any unemulsified silicone material and does not produce unemulsified silicone oil or polymers upon aging.

Further, the method of the instant invention has been found to be capable of producing emulsions which contain higher amounts of polysiloxane polymer than typically determined by the ring/chain equilibrium of the system. Conversion of cyclic siloxane to polysiloxane can range from values determined by the ring/chain equilibrium of the system to 100 percent. Essentially all of the cyclic siloxane is considered reacted when, at a minimum, values determined by the ring/chain equilibrium for the system are achieved.

The emulsions produced by the method of this invention are comprised of at least one silicone material, cationic or anionic (herein referred to as only ionic) surfactant, nonionic surfactant, catalyst and water. In some instances it is possible to have an ionic surfactant that can also act as the catalyst thereby giving an emulsion comprised of silicone, ionic surfactant, nonionic surfactant and water. In other instances, it is possible to have an ionic surfactant that has nonionic characteristics such that it behaves as a ionic and nonionic surfactant thereby giving an emulsion comprised of a silicone, ionic surfactant, catalyst and water.

The polymerization reaction employed in the method of this invention involves the opening of cyclic siloxane rings using an acid or base catalyst in the presence of water. Upon opening of the rings, polysiloxanes oligomers with terminal hydroxy groups are formed. These polysiloxane oligomers then react with each other or with other siloxane reactants that may be in the reaction medium, through a condensation reaction to form the polysiloxane polymers or copolymers. It is believed that these polymers precipitate and aggregate to form particles which are stabilized at a specific particle size in the water by the ionic and nonionic surfactants. The particle size is determined by the reaction parameters and the components used in forming the emulsions.

Polydiorganocyclosiloxanes which are useful in the method of this invention are those that are generally insoluble in water and can be readily polymerized using emulsion polymerization techniques. The preferred cyclic siloxanes are of the general formula



wherein each R is independently selected from a saturated or unsaturated alkyl group consisting of 1 to 6 carbon atoms, an aryl group consisting of 6 to 10 carbon atoms, wherein any of said R groups optionally contain a functional group which is unreactive in the ring opening and polymerization reaction; and x has a value of 3 to 7.

R may be further defined as methyl, ethyl, propyl, phenyl, allyl, vinyl, $-\text{R}^1-\text{F}$, where R^1 is selected from an alkylene group containing 1 to 6 carbon atom and an arylene group containing 6 to 10 carbon atoms; and F is a functional group such as an amine, diamine, halogen, carboxy, mercapto and others; and $-\text{R}^1-\text{F}^1-\text{R}$ wherein R^1 and R are as described above and F^1 is a non carbon atom such as oxygen, nitrogen or sulfur.

The cyclic siloxanes useful in the instant invention may be exemplified by compounds such as hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, tetramethyltetravinylcyclotetrasiloxane, or tetramethyltetraphenylcyclotetrasiloxane. Mixtures of the various cyclic siloxanes may also be used for the preparation of the emulsions.

It is feasible to produced copolymers through the emulsion polymerization reaction by having present in the reaction medium a small portion of other siloxane reactants. These siloxane reactants may be any compound that contains a hydrolyzable or silanol group and that is capable of polymerization using emulsion polymerization. It is preferred that these siloxane reactants comprise no more than 10 mole percent of the total silicone content.

Examples of the siloxane reactants include organofunctional siloxanes such as amine functional silanes, vinyl functional silanes, halogenalkyl functional silanes and hydroxy endblocked polysiloxanes. These siloxane reactants can be further exemplified by silanol terminated polydimethylsiloxanes with a degree of polymerization between 1 and 7, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, trimethoxyvinylsilane, tris-(2-methoxyethoxy)vinylsilane and

3-chloropropyltrimethoxysilane.

The emulsions produced by the method of this invention typically contain a silicone concentration of 10 to 70 percent by weight of the total emulsion solution. The preferred level of silicone is 25 to 60 percent by weight of the total emulsion solution. The larger the particle size, the higher the concentration of polysiloxane the emulsion may contain. Emulsions may be produced which contain less than 10 percent silicone content however, these emulsions typically hold little or no economic value.

The reaction to polymerize the silicones and form the emulsions is carried out in a reaction medium comprised of water, at least one ionic surfactant, at least one nonionic surfactant and a catalyst. Any catalyst that is capable of polymerizing cyclic siloxanes in the presence of water is useful in the method of the instant invention. Catalysts for the reaction include those catalysts which are known as condensation polymerization catalysts and are capable of cleaving siloxane bonds. Condensation polymerization catalysts known in the art include, but are not limited to, strong acids such as substituted benzenesulfonic acids, aliphatic sulfonic acids, hydrochloric acid and sulfuric acid and strong bases such as quaternary ammonium hydroxides and metal hydroxides. In some instances, ionic surfactants, such as dodecylbenzenesulfonic acid, can additionally function as the catalyst. Other useful catalytic systems include phase transfer catalysts such as tetrabutyl ammonium hydroxide or ion exchange resins whereby a catalyst may be formed in situ.

The catalyst is present in the reaction medium usually at levels of 0.01 to 30 percent by weight of the total silicone. Typically, the strong acids and basic metal hydroxides can be used within the lower end of this range while the ionic surfactants which also function as the catalyst will be present at the concentration on the higher end of this range.

The reaction medium must further comprise both an ionic AND a nonionic surfactant to stabilize the polysiloxane in the emulsion. Ionic surfactants may be selected from either a cationic or an anionic surfactant known in the art as useful in emulsion polymerization.

Suitable anionic surfactants include, but are not limited to, sulfonic acids and their salt derivatives. The anionic surfactants useful in the instant invention can be exemplified by, but are not limited to alkali metal sulforicnates; sulfonated glyceryl esters of fatty acids such as sulfonated monoglycerides of coconut oil acids; salts of sulfonated monovalent alcohol esters such as sodium oleylisethionate; amides of amino sulfonic acids such as the sodium salt of oleyl methyl tauride; sulfonated products of fatty acids nitriles such as palmitonitrile sulfonate; sulfonated aromatic hydrocarbons such as sodium alphanaphthalene monosulfonate; condensation products of naphthalene sulfonic acids with formaldehyde; sodium octahydroanthracene sulfonate; alkali metal alkyl sulfates, ether sulfates having alkyl groups of 8 or more carbon atoms and alkylarylsulfonates having 1 or more alkyl groups of 8 or more carbon atoms.

Anionic surfactants commercially available and useful in the instant invention include, but are not limited to, dodecylbenzenesulfonic acid sold under the name BIOSOFT® S-100 by STEPAN CO. and related salts such as the sodium salt of dodecylbenzenesulfonic acid sold under the name SIPONATE® DS-10 by ALCOLAC INC.

Cationic surfactants useful in the method of the instant invention are those known in the art to be useful in stabilization of emulsions produced via emulsion polymerization. These cationic surfactants include, but are not limited to, various fatty acid amines and amides and their derivatives and the salts of the fatty acid amines and amides. The cationic surfactants useful in the instant invention can be exemplified by, but are not limited to, aliphatic fatty amines and their derivatives such as dodecylamine acetate, octadecylamine acetate and acetates of the amines of tallow fatty acids; homologues of aromatic amines having fatty chains such as dodecylanalin; fatty amides derived from aliphatic diamines such as undecylimidazoline; fatty amides derived from disubstituted amines such as oleylaminodiethylamine; derivatives of ethylene diamine; quaternary ammonium compounds such as tallow trimethyl ammonium chloride, dioctadecyldimethyl ammonium chloride, didodecyldimethyl ammonium chloride and dihexadecyldimethyl ammonium chloride; amide derivatives of amino alcohols such as beta-hydroxyethylsterarylamide; amine salts of long chain fatty acids; quaternary ammonium bases derived from fatty amides of di-substituted diamines such as oleylbenzylaminoethylene diethylamine hydrochloride; quaternary ammonium bases of the benzimidazolines such as methylheptadecyl benzimidazol hydrobromide; basic compounds of pyridinium and its derivatives such as cetylpyridinium chloride; sulfonium compounds such as octadecylsulfonium methyl sulfate; quaternary ammonium compounds of betaine such as betaine compounds of diethylamino acetic acid and octadecylchloromethyl ether; urethanes of ethylene diamine such as the condensation products of stearic acid and diethylene triamine; polyethylene diamines; and polypropanolpolyethanol amines.

Cationic surfactants commercially available and useful in the instant invention include, but are not limited to ARQUAD® T27W, ARQUAD® 16-29, ARQUAD® C-33, ARQUAD® T50, ETHOQUAD® T/13 ACETATE, all manufactured by AKZO CHEMIE.

The ionic surfactant is typically present at levels of 0.05 to 30 percent by weight of the total emulsion. The preferred levels are from 0.5 to 20 percent by weight of the total emulsion.

Nonionic surfactants useful in the method of the instant invention are those that have a hydrophilic-lipophilic balance (HLB) between 10 and 20. Nonionic surfactants with an HLB of less than 10 may be used in the instant invention, however, a hazy solution may result due to the limited solubility of the nonionic surfactant in water. It is preferred that when using a nonionic surfactant with an HLB of less than 10, that a nonionic surfactant with an HLB of greater than

10 also be added during or after polymerization. The preferred nonionic surfactants are those which are stable in the polymerization environment.

The nonionic surfactants useful in method of the instant invention can be exemplified by, but not limited to, 2,6,8 trimethyl-4-nonyloxypolyethylene oxyethanol (6EO) (sold as TERGITOL® TMN-6 by UNION CARBIDE CORP.);
 5 2,6,8-trimethyl-4-nonyloxypolyethylene oxyethanol (10EO) (sold as TERGITOL® TMN-10 by UNION CARBIDE CORP.); alkyleneoxypolyethyleneoxyethanol (C 11-15, secondary alkyl, 7EO) (sold as TERGITOL® 15-S-7 by UNION CARBIDE CORP.); alkyleneoxypolyethyleneoxyethanol (C 11-15, secondary alkyl, 9EO) (sold as TERGITOL® 15-S-9 by UNION CARBIDE CORP.); alkyleneoxypolyethyleneoxyethanol (C 11-15, secondary alkyl, 15EO) (sold as TERGITOL® 15-S-15 by UNION CARBIDE CORP.); octylphenoxy polyethoxy ethanol (40EO) (sold as TRITON® X405 by
 10 ROHM and HAAS CO.) and nonylphenoxy polyethoxy ethanol (10EO) (sold as MAKON 10 by STEPAN CO.).

Levels of nonionic surfactant typically greater than 0 and less than 40 weight percent based on the weight of the total emulsion are useful in obtaining oil-free emulsions using the method of the instant invention. The preferable levels are from 0.5 to 30 weight percent based on the total weight of the emulsion.

Presently there are some commercially available ionic surfactants that have the characteristics of both the ionic
 15 and nonionic surfactants combined in the same compound. One such compound is sold by AKZO CHEMIE under the name of ETHOQUAD® 18/25 (methylpolyoxyethylene (15) octadecylammonium chloride). This compound is a cationic quaternary ammonium salt with polyethyleneoxide tails. When this type of ionic surfactant is used in the method of the instant invention, it is not necessary to have both the ionic and nonionic surfactant present in the reaction medium. Only the ionic surfactant having the nonionic characteristics is needed in the reaction medium. However, if the ionic
 20 surfactant does not have the characteristics of both the ionic and nonionic surfactants it is necessary to use both types of surfactants in the method of the instant invention. These types of surfactants are typically used in the emulsion at levels equal to the level of ionic surfactants used.

The method of this invention is carried out by creating a mixture comprising a cyclic siloxane, ionic surfactant, nonionic surfactant, water and catalyst. The mixture is then heated with agitation at a polymerization reaction temper-
 25 ature until essentially all of the cyclic siloxane is reacted and a stable, oil-free emulsion is formed. The time required for formation of the stable, oil-free emulsion will vary depending on the reactants and the reaction conditions.

The mixture of cyclic siloxane, ionic surfactant, nonionic surfactant, water and catalyst is not stable and will separate without some means of agitation. It is not necessary to have all of the cyclic siloxane fully dispersed into the mixture during the reaction however, some means of agitation must be provided throughout the course of the reaction.

Combining the cyclic siloxane, ionic surfactant, nonionic surfactant, water and catalyst and then reacting the cyclic
 30 siloxanes to form the emulsion can take place in several ways. The first of these ways is to combine all of the ingredients with agitation, in any given order and heat to the desired polymerization temperature with agitation thereby allowing the cyclic siloxanes to react and form an emulsion. Another way is to combine all of the ingredients with agitation, except for the catalyst, heat to the desired polymerization temperature, add the catalyst and thereafter heat and agitate
 35 at the desired polymerization temperature thereby allowing the cyclic siloxanes to react and form an emulsion. Another way is to combine all of the ingredients with agitation, except for the cyclic siloxane, heat to the desired polymerization temperature, add or feed in the cyclic siloxane and thereafter heat and agitate at the desired polymerization temperature thereby allowing the cyclic siloxanes to react and form an emulsion.

It is not essential that the ingredients used in producing the emulsions by the method of this invention be combined
 40 in any given order. However, it is essential to have agitation during and following the addition of the ingredients and to have achieved or to heat to the polymerization temperature when all of the ingredients have been combined.

The preferred method for forming the emulsions is to create a mixture by combining the cyclic siloxane or mixture of cyclic siloxanes, at least one nonionic surfactant, at least one ionic surfactant and water, providing agitation such that the cyclic siloxane is fully dispersed in the mixture; heating to the polymerization temperature; and adding the
 45 catalyst. The mixture is then held at the polymerization temperature with agitation until a stable, oil-free emulsion is formed.

Polymerization reaction temperatures useful in the method of the instant invention are typically above the freezing point but below the boiling point of water. Pressures above or below atmospheric pressure may allow operation outside of this range. At lower temperatures, especially those below room temperature, the polymerization reaction may pro-
 50 ceed more slowly. The preferred temperature range is to have a temperature of at least 50°C. but less than 95°C.

The polymerization reaction can be stopped at the desired level of conversion of cyclic siloxane and/or particle size by using methods known in the art. It is preferred to stop the reaction when the largest amount of cyclic siloxane has been reacted or when ring/chain equilibrium for the system and the desired particle size have been obtained. Reaction times of less than 24 hours and typically less than 5 hours, are sufficient to achieve the desired particle size
 55 and/or level of conversion. The methods for stopping the reaction typically encompass neutralization of the catalyst by the addition of equal or slightly greater stoichiometric amount of acid or base (depending upon the type of catalyst). Either a strong or weak acid/base may be used to neutralize the reaction. Care must be taken when using a strong acid/base not to over neutralize as it may be possible to re-catalyze the reaction. It is preferred to neutralize with

sufficient quantities of acid or base such that the resulting emulsion has a pH of less than 7 when a cationic surfactant is present and a pH of greater than 7 when an anionic surfactant is present.

By controlling certain operational parameters of the method of this invention it is possible to produce an emulsion of a specific type (standard, fine or micro) and further, to produce a desired particle size in the resulting emulsion. These operational parameters include reaction temperature, amount and type of ionic surfactant, amount and type of nonionic surfactant, amount of water, amount of catalyst and the optional presence of alcohols. The trends experienced when altering some of these parameters are not what would be typically expected by those skilled in the art.

It has been found when using the method of the instant invention, that increasing the reaction temperature increases the particle size of the polysiloxane. By holding the concentrations and types of reactants constant, it is feasible to produce different emulsions each with different particle sizes by altering the reaction temperature used in the production of each emulsion. For optimum particle size control it is preferred to add the catalyst into the mixture comprising the ionic surfactant, nonionic surfactant, cyclic siloxane and water after heating the mixture to the polymerization temperature.

It has also been found when using the method of the instant invention, that increasing the amount of the ionic surfactant decreases the particle size of the polysiloxane. The ionic surfactant present during the polymerization reaction appears to have the greatest effect on the particle size. Additional ionic surfactant added in the latter part of the polymerization reaction, just prior to or after neutralization, does not appear to greatly affect the particle size. Additional ionic surfactant is optionally added in the latter part of the polymerization reaction as a means for minimizing viscosity. It is possible to have equivalent amounts of ionic surfactant present in the final emulsion yet produce different particle sizes. This can be achieved by adding different amounts of ionic surfactant during the polymerization reaction and adding any additional amounts in the latter part of the polymerization reaction or just prior to neutralization. High levels of the ionic surfactant present during the polymerization reaction will often result in incomplete reactions and the failure to produce an oil-free emulsion. Levels of ionic surfactant which are too small may also cause similar effects. Those skilled in the art will be able to readily determine the levels of ionic surfactant needed to produce the desired emulsion.

The type of ionic surfactant used in forming the emulsion can also effect the particle size of the polysiloxane. Ionic surfactants can be classified by their hydrophilicity (HLB) or by the number of carbons in the alkyl group of the surfactant. By choosing an ionic surfactant with a higher degree of hydrophilicity and holding all other operational parameters constant, a larger particle size will result in the emulsion formed. A higher degree of hydrophilicity is often associated with shorter alkyl chains. An ionic surfactant with a lower degree of hydrophilicity will result in an emulsion with a smaller particle size. It is preferred to use ionic surfactants having an alkyl chain containing 8 or more carbon atoms.

The amount of nonionic surfactant can also be used to control the particle size in the emulsion. By increasing the amount of nonionic surfactant, the particle size is increased. It is preferred that most of the nonionic surfactant be present in the reaction medium during the polymerization reaction to have an effect on the particle size. It is necessary to have the nonionic surfactant present during the polymerization reaction to result in an oil-free emulsion.

The nonionic surfactants can be classified by the HLB factor. Nonionic surfactants may be further classified by their hydrocarbon segment. Using a nonionic surfactant having the same or almost the same type of hydrocarbon segment and having a larger HLB value will generally result in a smaller particle size. The structure of the hydrocarbon segment (i.e., linear, branched, aryl and combinations thereof) of the nonionic surfactant will also have some effect on the particle size of the emulsion formed.

The amount of water present during the polymerization of the siloxanes has also been found to effect the type of emulsion formed. Typically, higher quantities of water present during the reaction will result in a smaller particle size. Although it typically takes more water to produce emulsions with smaller particle sizes it is still feasible to produce micro or fine emulsions having relatively high polysiloxane concentrations. Fine and microemulsions produced by the method of the instant invention can contain 30% to 60% by weight of polysiloxane.

The amount of catalyst present during the polymerization reaction can result in varying particle sizes. It has been found that increasing the catalyst concentration can increase the particle size of the emulsion formed. The degree of effect that the catalyst concentration has on the particle size is dependent upon the type of ionic and nonionic surfactants used. With some surfactant systems, there may be an upper limit to the amount of catalyst that will result in an increased particle size. Above that limit, any additional catalyst added will not further increase the particle size.

A small quantity of alcohol can be added into the reaction medium before or after catalysis to increase the particle size of the emulsion. Alcohols useful in the method of the instant invention include methanol, ethanol and isopropanol. It is well known in the art that alcohols are typically used to break emulsions. Because of this, it is preferred to keep the concentration of the alcohol at low levels, more preferably below 5 percent by weight. To have the greatest effect on the particle size it is preferred to have the alcohol present throughout the course of the polymerization reaction.

By operating within the window outlined by the above mentioned parameters it is feasible to produce a stable emulsion free of oil. Since each operational parameter has an interactive effect relative to all other operational parameters it is not possible to give the exact limits for each. By interactive effect, it is meant that the value of one parameter is dependent upon the values of the other parameters. One skilled in the art would be able to readily determine the

limits on the operational parameters for the type of emulsion being produced based on the type and amounts of reactants and the reaction conditions. It is possible in the method of the instant invention to simultaneously change two operational parameters and negate the effect of each resulting in no change of particle size or type of emulsion formed.

It has also been found that using the method of this invention within the operating window outlined above and that by neutralizing the catalyst and thereby stopping the polymerization reaction at a certain point, cyclic siloxane conversions of up to 100 percent can be achieved. By allowing the reaction to continue beyond this point, cyclic siloxane will reform at levels approaching the values determined by the ring/chain equilibrium for the system. Thus, the method of this invention can allow for cyclic siloxane conversions greater than those determined by ring/chain equilibrium for the system. The reasons as to why higher level of cyclic siloxane conversion occurs is not quite understood however, an understanding is not necessary to practice the method of the instant invention. One skilled in the art will be able to determine the point at which to stop the reaction to achieve the higher levels of cyclic siloxane conversion using techniques known in the art which allow one to follow the polymerization reaction.

So that those skilled in the art can understand and appreciate the invention taught herein, the following examples are presented, being it understood that these examples should not be used to limit the scope of this invention over the limitations found in the claims attached hereto.

In the following examples particle size was determined using a particle size instrument using the principle of quasi-elastic light scattering and the cumulant method of D. E. Koppel {(J. Chem. Phys., 57, 4814(1972))}. Percent Conversion was determined using a weight loss method consisting of placing 2 grams of material in a oven at 105°C. for 2 hours. The calculation for determining percent conversion was the difference between the percent nonvolatile content and the percent non-silicone nonvolatile divided by the percent silicone all times 100.

Examples 1 through 10 illustrate the use of cationic and nonionic surfactants in the emulsion polymerization reaction of cyclic siloxanes and the effects of the various operating parameters. Example 11 illustrates the co-polymerization of a cyclic siloxane and a reactive silane using cationic and nonionic surfactants. Example 12 illustrates the use of a cationic surfactant that has the characteristics of both a cationic and a nonionic surfactant. Example 13 illustrates the process where a cationic/nonionic surfactant system is used and where the silicone is pre-emulsified prior to catalysis. Example 14 illustrates the use of an anionic surfactant that has the characteristics of both a anionic surfactant and a catalyst. Example 15 illustrates the effect of the amount of nonionic surfactant in the emulsion polymerization reaction of cyclic siloxanes using an anionic surfactant-catalyst. Example 16 illustrates the use of functionalized cyclic siloxanes in the process. Example 17 illustrates the process whereby a standard emulsion is produced. Example 18 illustrates the effect of agitation on the ability to produce the emulsions.

COMPARATIVE EXAMPLE 1

This example illustrates the method as taught in U.S. Patent No. 3,294,725, Example 1.

A solution of 150 grams of dimethylcyclsiloxane, 5 grams of the sodium salt of dodecylbenzenesulfonic acid, 2 grams of dodecylbenzenesulfonic acid and 333 grams of water were placed in a reactor, agitated vigorously by stirring and heated to 80°C. The reaction medium was held at 80°C. for 24 hours with continued stirring.

A sample was taken after 3 hours and neutralized. The result was a white emulsion having a particle size of 80 nanometers (nm) with a broad size distribution. After the sample was allowed to stand for several hours, there was observed to be 22% unemulsified oil on the top which indicated that only a small portion of the cyclic siloxane had reacted.

After 24 hours the product was neutralized. It was an opaque white emulsion having a particle size of 130 nm with a broad particle size distribution. After standing for several hours, there was observed to be 6% unemulsified oil on the top. Percent conversion of the reacted cyclic siloxane was determined to be 87%.

COMPARATIVE EXAMPLE 2

This example illustrates a method wherein only a cationic surfactant is used and the nonionic surfactant is not used.

450 grams of water, 184 grams of ARQUAD® T27W and 350 grams of cyclic siloxanes having an average of 4 Si atoms per molecule, were added with stirring to a reaction flask and heated to 75°C. 10 grams of 20% by weight sodium hydroxide was added to the mixture in the flask. The reaction was allowed to proceed for 3.5 hours before being neutralized with 5.8 grams of 85 percent concentrated phosphoric acid. The resulting product contained about 11% oil on top. The particle size was 136 nm, however, there was a large particle size distribution. The conversion of monomer was 79% by weight.

The same emulsion was produced according to the method of this invention by additionally using 95 grams of MAKON® 10 (see Example 1). This emulsion was oil free and had a particle size of 35 nm and a conversion of monomer of 95%.

COMPARATIVE EXAMPLE 3

This example further shows the elimination of the nonionic surfactant.

600 grams water, 35 grams of ARQUAD® T27W and 350 grams of cyclic siloxanes having an average of 4 Si atoms per molecule, were added with stirring to a reaction flask and heated to 95°C. 10 grams of 20% by weight sodium hydroxide was added to the mixture in the flask. The reaction was allowed to proceed for 3.5 hours before being neutralized with 5.8 grams of 85 percent concentrated phosphoric acid. The resulting product contained about 13% oil on top. The particle size was 153 nm. The conversion of monomer was 81% by weight.

The same emulsion was produced according to the method of this invention by additionally using 30 grams of MAKON® 10. The emulsion was oil free, had a particle size of 118 nm and the conversion of monomer was 84% by weight.

COMPARATIVE EXAMPLE 4

This example illustrates a method wherein only an anionic surfactant is used and the nonionic surfactant is not used.

350 grams of water and 200 grams of cyclic siloxanes having an average of 4 Si atoms per molecule, were added with stirring to a reaction flask and heated to 95°C. 50 grams of dodecylbenzenesulfonic acid was added to the mixture in the flask. The reaction was allowed to proceed for 17 minutes before it became too viscous to stir. The particle size was 53 nm however, there was a large particle size distribution. The conversion of monomer was not determined. The same emulsion was produced according to the method of this invention by additionally using 20 grams of TRITON X405. The mixture did not become too viscous and was allowed to react for 4 hours. The emulsion was oil free, had a particle size of 82 nm and the conversion of monomer was 93%.

EXAMPLE 1

This example illustrates a typical procedure of this invention wherein all of the surfactant is added at the beginning of the experiment.

354.9 grams of water, 95 grams of MAKON 10, 184 grams of ARQUAD® T27W and 350 grams of cyclic siloxanes having an average of 4 Si atoms per molecule, were added with stirring to a reaction flask and heated to 75°C. 10 grams of 20% by weight sodium hydroxide was added to the mixture in the flask. The reaction was allowed to proceed for 2.5 hours with stirring before being neutralized with 5.8 grams of 85 percent concentrated phosphoric acid. The resulting product was an oil free, microemulsion with a 38 nanometer (nm) particle size. The conversion of monomer was 95% by weight. After 16 months at room temperature the microemulsion was still oil-free and had a particle size of 40 nm.

EXAMPLE 2

This example illustrates a typical method of this invention wherein all of the nonionic and part of the cationic surfactant is added at the beginning of the reaction and another part is added after catalysis.

354.9 grams of water, 95 grams of MAKON® 10 and 350 grams of cyclic siloxanes having an average of 4 Si atoms per molecule, were added to a reaction flask with stirring and heated to 65°C. 150 grams of ARQUAD® T27W and 10 grams of 20% by weight sodium hydroxide was added to the mixture in the flask. After the reaction had proceeded for 45 minutes an additional 34 grams of ARQUAD® T27W was added to minimize the viscosity. The reaction was stopped after 2 hours and 45 minutes by neutralization with 5.8 grams of 85 percent concentrated phosphoric acid. An oil-free microemulsion with a particle size of 31nm was formed. Percent conversion of monomer was not determined. After 17 months at room temperature the microemulsion was oil free and had a particle size of 30 nm.

EXAMPLE 3

This example illustrates the effect of the reaction temperature on the particle size.

The reaction was carried out by combining, with stirring, in a reaction flask 355 grams of water, 95 grams of MAKON® 10, 140 grams of ARQUAD® T27W and 350 grams cyclic siloxanes having an average of 4 Si atoms per molecule. The contents in the flask were heated to the desired temperature (Table 1). 10 grams of 20% by weight sodium hydroxide was added to the mixture in the flask. The reaction was allowed to proceed until the monomer was consumed or the system was in equilibrium. The catalyst was neutralized by the addition of 5.8 grams of 85 percent concentrated phosphoric acid. In runs 3 and 4 an additional 44 grams of ARQUAD® T27W was added in the latter part of the reaction to minimize viscosity. In run 5 only 34 grams of the ARQUAD® T27W was added. Particle size and conversion results are given in Table 1. The microemulsions were all oil-free. After 16 months at room temperature,

the microemulsions were oil-free and had a particle size of 36nm (Run 3), 48 nm (Run 4) and 51 nm (Run 5).

Table 1

Run No.	3	4	5
Temperature (°C.)	65	70	75
Particle Size (nm)	34	45	50
Percent Conversion	85	98	100
Reaction Time (hrs.)	5	4	5

EXAMPLE 4

This example illustrates the effect of concentration of cationic surfactant on the particle size of the emulsion formed. The procedure used is the same as used in Example 3. All reactions were run at 65°C. In Run 6, an additional 34 grams of ARQUAD® T27W was added 1.5 hours after catalysis to minimize viscosity. In Run 7, an additional 34 grams of ARQUAD® T27W was added 45 minutes after catalysis to minimize the viscosity. In Run 8, no additional ARQUAD® T27W was added after catalysis. Operating Parameters and results are given in Table 2. The microemulsions were all oil free. After 16 months at room temperature, the microemulsions were oil-free and had a particle size of 32 nm (Run 6), 30 nm (Run 7) and 28 nm (Run 8).

Table 2

Run No.	6	7	8
ARQUAD® T27W (g)	140	150	184
MAKON® 10 (g)	95	95	95
Cyclic siloxane (g)	350	350	350
Water (g)	355	355	355
20% NaOH (g)	10	10	10
Particle Size (nm)	34	31	27
Percent Conversion	100	nd	nd
Reaction Time	6	4	2
nd = not determined			

EXAMPLE 5

This example illustrates the effect of concentration of the nonionic surfactant on the particle size of the emulsion formed. The procedure used is the same as used in Example 3. Two different types of nonionic surfactants were evaluated at different concentrations (MAKON® 10 and TERGITOL® 15S7). No additional cationic surfactant was added during the course of the polymerization. In runs 12 and 13, 95 and 44 grams of water, respectively, was added after neutralization. In runs 9-11, the amount of water used is adjusted to compensate for the additional MAKON® 10 being added. Operating Parameters and results are given in Table 3. The microemulsions and the fine emulsion contained no free oil. After 1 year at room temperature, the micro-emulsions and the fine emulsion contained no free oil and had a particle size of 27 nm (Run 9), 32 nm (Run 10), 41 nm (Run 11) and 165 nm (Run 13).

Table 3

Run No.	9	10	11	12	13
ARQUAD® T27W	210	210	210	140	140
MAKON® 10 (g)	75	85	95	--	--
TERGITOL® 15S7 (g)	--	--	--	60	95
Cyclic siloxane (g)	350	350	350	350	350
Water (g)	349	339	329	355	355
20% NaOH (g)	10	10	10	10	10
Temperature	75	75	75	65	65
Particle Size (nm)	26	32	39	63	158
Percent Conversion	85	84	95	99	95

Table 3 (continued)

Run No.	9	10	11	12	13
Reaction Time	2.5	2.5	4	4	2.5

EXAMPLE 6

This example illustrates the effect of concentration of water on the particle size of the emulsion formed. The procedure used is the same as used in Example 3. Two different reaction temperatures (95°C. and 70°C.) were evaluated at varying water concentrations. Operating Parameters and results are given in Table 4. The oil formed in runs 15 to 16 illustrate examples where the water concentration is, respectively, at the edge of and outside the operating window of the invention. Runs 14, 17 and 18 are inside the operating window producing emulsions with no free oil. The fine emulsion produced in run 14 had no free oil after 6 months at room temperature. The microemulsion produced in run 17 had no free oil after 16 months at room temperature and had a particle size of 33 nm. The microemulsion produced in run 18 had no free oil after 1 year at room temperature. No further oil developed in the fine and microemulsions produced in runs 15 and 16.

Table 4

Run No.	14	15	16	17	18
ARQUAD® T27W	17	17	17	184	184
MAKON® 10 (g)	17	17	17	95	95
Cyclic siloxane (g)	350	350	350	350	350
Water (g)	180	250	290	355	522
20% NaOH (g)	10	10	10	10	10
Temperature	95	95	95	70	70
Particle Size (nm)	241	162	131	33	25
Percent Oil	0	trace	3	0	0
Percent Conversion	nd	84	86	97	88
Reaction Time	2	3	3	6	6
nd = not determined					

EXAMPLE 7

This example illustrates the effect of HLB of the nonionic surfactant on the particle size of the emulsion formed. The procedure used is the same as used in Example 3. All reactions were run at 65°C. During Runs 20-22, an additional 44 grams of ARQUAD® T27W was added in the latter part of the polymerization to minimize viscosity. Operating Parameters and results are given in Table 5. Comparing runs 20 and 22 shows the effect of different hydrocarbon groups on surfactants with similar HLB's. The fine and microemulsions contained no free oil. The fine emulsion produced in run 19 had no free oil after 15 months at room temperature and had a particle size of 165 nm. After 10 months at room temperature, the microemulsion produced in run 20 was oil-free and had a particle size of 69. The microemulsions produced in runs 21 and 22 were oil-free after 16 months at room temperature and had a particle size of 37 nm and 32 nm, respectively.

Table 5

Run No.	19	20	21	22
ARQUAD® T27W (g)	140	140	140	140
Nonionic Surf. (g)	95	95	95	95
Type Nonionic*	T15S7	T15S9	T15S12	MAKON®10
HLB	12.2	13.3	14.5	13
Cloud Point	37	60	90	54
Cyclic siloxane (g)	350	350	350	350
Water (g)	355	355	355	355

*T=TERGITOL

nd = not determined

Table 5 (continued)

Run No.	19	20	21	22
20% NaOH (g)	10	10	10	10
Temperature	65	65	65	65
Particle Size (nm)	158	64	34	34
Percent Conversion	95	96	nd	85
Reaction Time	2.5	6	2.5	5

EXAMPLE 8

This example illustrates the effect of the type of cationic surfactant on the particle size of the emulsion formed. The procedure used is the same as used in Example 3. All reactions were run at 70°C. No additional cationic surfactant was added in the latter part of the polymerization. All emulsions were prepared using 50 grams of actual cationic surfactant (they are available in varying concentrations). The amount of water added was adjusted according to the amount of water in the surfactant such that all emulsion were prepared using a total of 489 grams of water. Operating Parameters and results are given in Table 6. Run 26 is considered to have failed since the cyclic siloxane conversion did not achieve at least ring/chain equilibrium, however, there was no unemulsified oil. The low conversion of cyclic siloxanes is believed to have been caused by the type of cationic surfactant in which the alkyl group was too short. The microemulsions produced in runs 23-25 were all oil free. After 15 months at room temperature, the microemulsions produced in runs 23 and 24 were oil free and had a particle size of 33 and 38 nm, respectively. After 1 year at room temperature, the microemulsion produced in run 25 contained no free oil. After 11 months, the standard emulsion produced in run 26 was oil free and had a particle size of 1158 nm.

Table 6

Run No.	23	24	25	26
Cationic Surf. (g) (diluted in water)	184	172	152	62.5
Type Cationic*	A-T27W	A16-29	A-C33	A-L8-80MS
Alkyl Group	C17	C16	C12	C8
MAKON® 10	95	95	95	95
Cyclic siloxane (g)	350	350	350	350
Water (g)	355	367	387	476.4
20% NaOH (g)	10	10	10	10
Temperature	70	70	70	70
Particle Size (nm)	33	35	92	1206
Percent Conversion	97	93	96	19
Reaction Time	6	2.5	4	

*A = ARQUAD®

EXAMPLE 9

This example illustrates the effect of the addition of alcohols into the reaction medium on the particle size of the emulsion formed. The procedure used is the same as used in Example 3. All reactions were run at 70°C. No additional cationic surfactant was added in the latter part of the reaction. Operating Parameters and results are given in Table 7. The 36 grams of isopropanol reported in Run 28 was present in the cationic surfactant (ARQUAD® T50) and was not an additional amount added into the reaction medium. The fine and microemulsions contained no free oil. After 15 months at room temperature, the micro and fine emulsions produced in runs 27 and 28 contained no free oil and had a particle size of 33 nm and 298 nm, respectively. After 11 months at room temperature, the microemulsion run 29 was oil-free.

Table 7

Run No.	27	28	29
Cationic Surf. (g)	184	100	184

Table 7 (continued)

Run No.	27	28	29
Type Cationic*	T27W	T50	T27W
MAKON® 10	95	95	95
Cyclic siloxane (g)	350	350	350
Water (g)	355	439	350
20% NaOH (g)	10	10	10
Temperature	70	70	70
Isopropanol	0	36	5
Particle Size (nm)	33	290	45
Percent Conversion	97	88	98
Reaction Time	6	5.5	4

* All are ARQUAD®

EXAMPLE 10

This example illustrates the effect of the catalyst concentration on the particle size of the emulsion formed. The procedure used is the same as used in Example 3. No additional cationic surfactant was added in the latter part of the reaction. Operating Parameters and results are given in Table 8. Runs 30 and 31 used ETHOQUAD® T/13 ACETATE and TERGITOL® 15S12 as the cationic and nonionic surfactants. Runs 32-34 used ARQUAD® T27W and MAKON® 10 as the cationic and nonionic surfactants. The microemulsions contained no free oil. After 2 months at room temperature, the microemulsions produced in runs 30 and 31 were oil-free. After 1 month at room temperature, the microemulsions produced in runs 32 to 34 were oil-free.

TABLE 8

Run No.	30	31	32	33	34
Cationic Surf. (g)	103	103	184	184	184
Type Cationic*	T/13	T/13	T27W	T27W	T27W
TERGITOL® 15S12	47	47	0	0	0
MAKON® 10	0	0	95	95	95
Cyclic siloxane (g)	300	300	350	350	350
Water (g)	350	350	362	361	360
50% NaOH (g)	2.1	1.5	3	4	5
Temperature	95	95	70	70	70
Particle Size (nm)	80	70	38	42	43
Percent Conversion	90	89	89	87	86
Reaction Time	4	4	4	4	4

*T/13 = ETHOQUAD® T/13 ACETATE

T27W = ARQUAD® T27W

EXAMPLE 11

This example shows the use of cyclic siloxanes and a aminofunctional silane such that there is copolymerization of the two silanes.

The reaction was carried out using the same method as in Example 3. No additional cationic surfactant was added in the latter part of the polymerization. In run 35, the aminofunctional silane was added 1 hour after catalysis. In run 36 the aminofunctional silane was added before catalysis. Reaction Conditions and Results are given in Table 9. N-(2-aminoethyl)-3-aminopropyltrimethoxysilane was used in runs 35 and 36.

It is believed that the larger particle size in run 36 resulted from the formation of alcohol during the hydrolysis of the aminofunctional siloxane. If the aminofunctional silane is added after catalysis and the reaction of cyclics is underway the alcohol formed does not appear to effect the particle size (see run 27 for comparison). The microemulsions contained no free oil. After 13 months at room temperature, the microemulsion produced in run 35 was oil free. After 15 months at room temperature, the microemulsion produced in run 36 was oil free and had a particle size of 48 nm.

Table 9

Run No.	35	36
ARQUAD® T27W (g)	184	184
MAKON® 10	95	95
Cyclic Siloxane (g)	346	346
Aminofunct. Silane (g)	6.5	6.5
Water (g)	355	352
20% NaOH (g)	10	10
Temperature	70	70
Particle Size (nm)	33	46
Percent Conversion	96	78
Reaction Time	4	3

EXAMPLE 12

This example shows the use of a cationic surfactant that has the characteristics of both a cationic and a nonionic surfactant in the same compound.

483.9 grams of water, 150 grams of ETHOQUAD® 18/25 (cationic/nonionic surfactant) and 350 grams of cyclic siloxanes with an average of 4 Si atoms per molecule, were combined, with stirring, in a reaction flask and heated to 70°C. 10 grams of 20% sodium hydroxide was added to the mixture in the flask with agitation. The reaction was allowed to proceed for 3.5 hours before neutralizing the catalyst with 5.8 grams of 85 percent concentrated phosphoric acid. An oil-free microemulsion having a particle size of 51 nm resulted. An 85% conversion of monomer was achieved. After 15 months at room temperature, the microemulsion was oil-free.

EXAMPLE 13

This example illustrates the process where the silicone is pre-emulsified prior to catalysis.

60 grams of TERGITOL® 15S9 was dissolved in 340 grams of water while stirring. 600 grams of cyclic siloxanes were added and mixed for another 15 minutes. This mixture was passed through a sonolator once at 1300 psi to produce an emulsion having 346nm particle size.

416.7 grams of the emulsion produced above was placed in a flask. While stirring, 307.5 grams water, 220 grams ARQUAD® T27W and 40 grams TERGITOL® 15S9 and 10 grams of 20% sodium hydroxide were added to the emulsion. This was immediately heated to 75°C. and held for 5 hours. The catalyst was neutralized with 5.8 grams of 85% concentrated phosphoric acid. The resulting microemulsion had a particle size of 53 nanometers and contained no free oil. After 18 months at room temperature, the microemulsion contained no free oil and had a particle size of 51 nm.

EXAMPLE 14

This example shows the use of an anionic surfactant that has the characteristics of both an anionic surfactant and a catalyst in the same compound.

615.7 grams of water, 80 grams of TRITON® X405 and 200 grams of cyclic siloxanes with an average of 4 Si atoms per molecule, were combined, with stirring, in a reaction flask and heated to 70°C. 50 grams of dodecylbenzenesulfonic acid (DBSA) was added to the mixture in the flask with agitation. The reaction was allowed to proceed for 19 hours before neutralizing the catalyst with 54 grams of triethanolamine. An oil-free microemulsion having a particle size of 79nm resulted. A 93% conversion of monomer was achieved. After 15 months at room temperature, the microemulsion contained no free oil and had a particle size of 73 nm.

EXAMPLE 15

This example illustrates the use of an anionic surfactant and the effects of varying the amount of nonionic surfactant. The procedure is the same as in Example 14. Results are given in Table 10. The fine and microemulsions contained no free oil. After 4 months at room temperature, the fine and microemulsions produced in runs 40 to 42 were oil-free. After 3 months at room temperature, the microemulsion produced in run 43 was oil-free.

Table 10

Run No.	40	41	42	43
TRITON® X405	80	40	20	10
Cyclic Siloxane (g)	200	200	200	200
Water (g)	350	350	350	350
DBSA (g)	50	50	50	50
Temperature	95	95	95	95
Particle Size (nm)	173	124	82	52
Percent Conversion	95	96	93	nd
Reaction Time	4	4	4	2
nd = not determined				

EXAMPLE 16

This example illustrates the use of a functionalized cyclic siloxane in the process. The cyclic siloxane contains methyl and vinyl functionality.

315.6 grams of water, 56 grams of MAKON® 10, 112 grams of ARQUAD® T27W and 210 grams of cyclic siloxanes having an average of 4 Si atoms per molecule and containing at least one vinyl group per Si atom, were added with stirring to a reaction flask and heated to 70°C. 2.10 grams of 50% by weight sodium hydroxide was added to the mixture in the flask. The reaction was allowed to proceed for 4 hours before being neutralized with 4.1 grams of 85 percent concentrated phosphoric acid. The resulting product was an oil free microemulsion with a 50 nm particle size. The conversion of monomer was 84% by weight. After 1 month at room temperature, the microemulsion was oil-free.

EXAMPLE 17

This example illustrates using the process to produce a standard emulsion.

1336 grams of water, 14 grams of MAKON® 10, 14 grams of ARQUAD® T27W and 245 grams of cyclic siloxanes having an average of 4 Si atoms per molecule, were added with stirring to a reaction flask and heated to 95°C. 2.8 grams of 50% by weight sodium hydroxide was added to the mixture in the flask. The reaction was allowed to proceed for 2 hours before being neutralized with 2.17 grams of glacial acetic acid. The resulting product was an oil free standard emulsion with a 401 nm particle size. The conversion of monomer was 86% by weight. After 1 month at room temperature, the emulsion was free of oil.

EXAMPLE 18

This example illustrates the effects of agitation on the process for making the emulsions.

248.4 grams of water, 66.5 grams of MAKON® 10, 128.8 grams of ARQUAD® T27W and 245 grams of cyclic siloxanes having an average of 4 Si atoms per molecule, were added with stirring to a reaction flask and heated to 70°C. 2.8 grams of 50% by weight sodium hydroxide was added to the mixture in the flask. The contents were mixed at an agitator speed of 100 RPM. After 1/2 hour, there was a small layer (approximately 6.4 mm (1/4 inch)) of cyclic siloxanes on the top of the reaction mixture. This layer slowly decreased in size with time until it disappeared. The reaction medium was neutralized after 20 hours with 4.1 grams of 85% concentrated phosphoric acid. An additional 103 grams of water was added to dilute emulsion to the desired solids level. The resulting product was an oil free microemulsion with a 42 nm particle size. After three days at room temperature, there was no free oil present.

The same emulsion as above was prepared at an agitator speed of 300 RPM. There was no undispersed oil in the reaction medium throughout the course of the reaction. The resulting product was an oil free microemulsion with a 34 nm particle size. After three days at room temperature there was no free oil present.

Claims

1. A method for producing stable, oil free polysiloxane emulsions comprising the steps of:

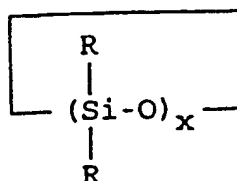
(A) preparing a mixture comprising:

- i) a cyclic siloxane or a mixture of cyclic siloxanes,
- ii) a nonionic surfactant or a mixture of nonionic surfactants,
- iii) a ionic surfactant or a mixture of ionic surfactants,
- iv) water, and
- v) a condensation polymerization catalyst

wherein said cyclic siloxane or mixture of cyclic siloxanes have not been mechanically pre-emulsified prior to addition into the mixture (A)

(B) thereafter heating and agitating the mixture at a polymerization reaction temperature until essentially all cyclic siloxane is reacted, whereby a stable, oil-free emulsion is formed.

2. A method as claimed in claim 1 wherein additionally the mixture is heated to the polymerization reaction temperature prior to the addition of the catalyst into the mixture.
3. A method as claimed in claim 1 wherein additionally the mixture is heated to the polymerization reaction temperature prior to the addition of the cyclic siloxane or mixture of cyclic siloxanes into the mixture.
4. A method as claimed in claim 1 wherein the ionic surfactant also functions as the catalyst.
5. A method as claimed in claim 1 wherein the cyclic siloxane or mixture of cyclic siloxanes are selected from



wherein each R is independently selected from a saturated or unsaturated alkyl group consisting of 1 to 6 carbon atoms and an aryl group consisting of 6 to 10 carbon atoms, wherein any of said R groups optionally contain a functional group which is unreactive in the ring opening and polymerization reaction; and x has a value of 3 to 7.

6. A method as claimed in claim 5 wherein the cyclic siloxane is octamethylcyclotetrasiloxane.
7. A method as claimed in claim 1 wherein the ionic surfactant is selected from cationic and anionic surfactants.
8. A method as claimed in claim 1 wherein the ionic surfactant is structurally such that it also functions as the nonionic surfactant.
9. A method as claimed in claim 1 wherein the mixture formed in (I) additionally contains siloxane reactants.
10. Use of a method according to one of claims 1 to 9 to produce an emulsion having a desired particle size.
11. Use in accordance with claim 10 wherein the control is provided by varying at least one operational parameter selected from reaction temperature, amount of ionic surfactant, type of ionic surfactant, amount of nonionic surfactant, type of nonionic surfactant, amount of water, amount of catalyst, and optional presence of an alcohol.
12. Use in accordance with claim 11 wherein the particle size is controlled by adjusting the temperature.
13. Use in accordance with claim 11 wherein the particle size is controlled by adjusting the amount of ionic surfactant.
14. Use in accordance with claim 11 wherein the particle size is controlled by adjusting the hydrophilic-lipophilic balance of the ionic surfactant.
15. Use in accordance with claim 11 wherein the particle size is controlled by adjusting the amount of the nonionic surfactant.

16. Use in accordance with claim 11 wherein the particle size is controlled by adjusting the amount of water.
17. Use in accordance with claim 11 wherein the particle size is controlled by adjusting the amount of catalyst.

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Patentansprüche

1. Verfahren zur Herstellung von stabilen, ölfreien Polysiloxanemulsionen umfassend die Stufen, daß man:

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(A) eine Mischung herstellt, die

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- i) ein cyclisches Siloxan oder eine Mischung von cyclischen Siloxanen,
- ii) ein nicht-ionisches Tensid oder eine Mischung nicht-ionischer Tenside,
- iii) ein ionisches Tensid oder eine Mischung ionischer Tenside,
- iv) Wasser und
- v) einen Kondensationspolymerisationskatalysator

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umfaßt, wobei das cyclische Siloxan oder die Mischung cyclischer Siloxane nicht mechanisch vor der Zugabe zu der Mischung (A) voremulgiert wurden,

(B) danach die Mischung auf eine Polymerisationsreaktionstemperatur erhitzt und bewegt, bis im wesentlichen das gesamte cyclische Siloxan reagiert hat, wobei eine stabile, ölfreie Emulsion gebildet wird.

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2. Verfahren nach Anspruch 1, worin zusätzlich die Mischung vor der Zugabe des Katalysators zu der Mischung auf die Polymerisationsreaktionstemperatur erhitzt wird.

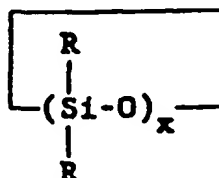
3. Verfahren nach Anspruch 1, worin zusätzlich die Mischung vor der Zugabe des cyclischen Siloxans oder der Mischung cyclischer Siloxane zu der Mischung auf die Polymerisationsreaktionstemperatur erhitzt wird.

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4. Verfahren nach Anspruch 1, worin das ionische Tensid auch als Katalysator dient.

5. Verfahren nach Anspruch 1, worin das cyclische Siloxan oder die Mischung cyclischer Siloxane ausgewählt ist aus

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worin jeder Rest R unabhängig ausgewählt ist aus gesättigten oder ungesättigten Alkylgruppen mit 1 bis 6 Kohlenstoffatomen und einer Arylgruppe mit 6 bis 10 Kohlenstoffatomen, wobei jede der Gruppen R gegebenenfalls eine funktionelle Gruppe enthalten kann, die bei der Ringöffnung und der Polymerisationsreaktion nicht reagiert; und x einen Wert von 3 bis 7 hat.

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6. Verfahren nach Anspruch 5, worin das Cyclosiloxan Octamethylcyclotetrasiloxan ist.

7. Verfahren nach Anspruch 1, worin das ionische Tensid ausgewählt ist aus kationischen und anionischen Tensiden.

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8. Verfahren nach Anspruch 1, worin das ionische Tensid eine solche Struktur hat, daß es auch als nichtionisches Tensid dient.

9. Verfahren nach Anspruch 1, worin die in (I) gebildete Mischung zusätzlich Siloxanreaktanten enthält.

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10. Verwendung eines Verfahrens nach einem der Ansprüche 1 bis 9, um eine Emulsion mit einer gewünschten Teilchengröße zu erzeugen.

11. Verwendung nach Anspruch 10, worin die Kontrolle erfolgt, indem mindestens ein Betriebsparameter ausgewählt

aus der Reaktionstemperatur, der Menge an ionischem Tensid, der Art des ionischen Tensids, der Menge an nicht-ionischem Tensid, der Art des nicht-ionischen Tensids, der Menge an Wasser, der Menge an Katalysator und der fakultativen Gegenwart eines Alkohols variiert wird.

- 5 12. Verwendung nach Anspruch 11, worin die Teilchengröße durch Einstellen der Temperatur kontrolliert wird.
13. Verwendung nach Anspruch 11, worin die Teilchengröße durch Einstellen der Menge an ionischem Tensid kontrolliert wird.
- 10 14. Verwendung nach Anspruch 11, worin die Teilchengröße durch Einstellen des hydrophilen/lipophilen Gleichgewichts des ionischen Tensids kontrolliert wird.
- 15 15. Verwendung nach Anspruch 11, worin die Teilchengröße durch Einstellen der Menge an nicht-ionischem Tensid kontrolliert wird.
16. Verwendung nach Anspruch 11, worin die Teilchengröße durch Einstellen der Wassermenge kontrolliert wird.
17. Verwendung nach Anspruch 11, worin die Teilchengröße durch Einstellen der Menge an Katalysator kontrolliert wird.
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Revendications

- 25 1. Procédé de préparation d'émulsions de polysiloxanes, exemptes d'huile, stables, comprenant les étapes de :

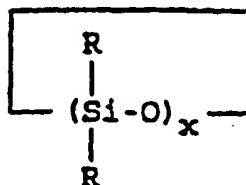
(A) préparation d'un mélange comprenant :

- 30 i) un siloxane cyclique ou un mélange de siloxanes cycliques,
 ii) un agent tensioactif non ionique ou un mélange d'agents tensioactifs non ioniques,
 iii) un agent tensioactif ionique ou un mélange d'agents tensioactifs ioniques,
 iv) eau, et
 v) un catalyseur de polymérisation par condensation

35 ledit siloxane cyclique ou mélange de siloxanes cycliques n'ayant pas été préémulsifié mécaniquement avant l'addition dans le mélange (A)

(B) puis de chauffage et d'agitation du mélange à une température de réaction de polymérisation jusqu'à ce qu'essentiellement tout le siloxane cyclique ait réagi, de sorte qu'une émulsion stable, exempte d'huile est formée.

- 40 2. Procédé selon la revendication 1, dans lequel, en plus, le mélange est chauffé à la température de réaction de polymérisation avant l'addition du catalyseur dans le mélange.
3. Procédé selon la revendication 1, dans lequel, en plus, le mélange est chauffé à la température de réaction de polymérisation avant l'addition du siloxane cyclique ou du mélange de siloxanes cycliques dans le mélange.
- 45 4. Procédé selon la revendication 1, dans lequel l'agent tensioactif ionique fonctionne aussi en tant que catalyseur.
5. Procédé selon la revendication 1, dans lequel le siloxane cyclique ou le mélange de siloxanes cycliques est choisi parmi
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où chaque R est indépendamment choisis parmi un groupe alkyle saturé ou insaturé constitué de 1 à 6 atomes de carbone et un groupe aryle constitué de 6 à 10 atomes de carbone, un ou plusieurs desdits groupes R contenant facultativement un groupe fonctionnel qui n'est pas réactif dans la réaction d'ouverture de cycle et de polymérisation ; et x a une valeur de 3 à 7.

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6. Procédé selon la revendication 5, dans lequel le siloxane cyclique est l'octaméthylcyclotétrasiloxane.

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7. Procédé selon la revendication 1, dans lequel l'agent tensioactif ionique est choisi parmi les agents tensioactifs cationiques et anioniques.

8. Procédé selon la revendication 1, dans lequel l'agent tensioactif ionique est structuralement tel qu'il sert aussi d'agent tensioactif non ionique.

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9. Procédé selon la revendication 1, dans lequel le mélange formé en (I) contient en plus des réactifs siloxanes.

10. Utilisation d'un procédé selon l'une quelconque des revendications 1 à 9 pour produire une émulsion ayant une taille de particules souhaitée.

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11. Utilisation selon la revendication 10, dans laquelle le témoin est fourni en faisant varier au moins un paramètre opératoire choisi parmi la température de réaction, la quantité d'agent tensioactif ionique, le type d'agent tensioactif ionique, la quantité d'agent tensioactif non ionique, le type d'agent tensioactif non ionique, la quantité d'eau, la quantité de catalyseur et la présence facultative d'un alcool.

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12. Utilisation selon la revendication 11, dans laquelle la taille des particules est ajustée en réglant la température.

13. Utilisation selon la revendication 11, dans laquelle la taille des particules est ajustée en réglant la quantité d'agent tensioactif ionique.

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14. Utilisation selon la revendication 11, dans laquelle la taille des particules est ajustée en réglant l'équilibre hydrophile-lipophile de l'agent tensioactif ionique.

15. Utilisation selon la revendication 11, dans laquelle la taille des particules est ajustée en réglant la quantité de l'agent tensioactif non ionique.

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16. Utilisation selon la revendication 11, dans laquelle la taille des particules est ajustée en réglant la quantité d'eau.

17. Utilisation selon la revendication 11, dans laquelle la taille des particules est ajustée en réglant la quantité de catalyseur.

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